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Epitaxial Growth of n-Tetracontane Obseved by High Resolution Electron Microscopy †

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Vopor deposited epitaxial films of n-tetracontane on the (001) of alkali halides were investigated by high resolution electron microscopy. A strange domain morphology, where n-tetracontane crystallized with the same orientation in the domain, was observed on the (001) of KCl. The terrace structure of KCl revealed by gold decoration method seems to cause the domain morphology.

High resolution imaging of the 001-lattice planes have revealed single-layers of paraffin molecules at the edges of the crystals, which may act as active sites during the crystal growth. Frequent appearance of such single-layer of molecules suggests the importance of step-by-step crystal growth of the paraffin crystals. On the coalescence, the small crystallites jointed together into a large crystallite without changing their crystal orientation in total, but the lattice fringes are deformed at the boundary of coalescence so as to minimize the interfacial energy.

KEY WORDS: n-tetracontane / Epitaxial growth / Domain morphology/ High resolution imaging / Single-layer of molecules / Coalescence

INTRODUCTION

There have been many efforts for imaging the crystal structures of paraffins and the related polyethylene [1-4] by high resolution electron microscopy in spite of their severe radiation damage by electron bombardment, because basic information on local structure (distortion of lattices, dislocations etc.) is expected to be obtained in such images of the typical long chain compounds. For these purposes, the efforts have been focused mainly on resolving each long molecules as projections along the chain axis, that is, to resolve hk0-spacings. Unfortunately the images observed so far are still inadequate to discuss the local structures of such crystal at a molecular level resolution, because it is hard to discern the molecular images directly on micrographs. On the other hand, the 001-lattice spacings of paraffin crystals are much longer than the hk0-spacings, therefore in the case of paraffins, the lattice images of the 001-spacings can be obtained more easily even with a conventional transmission electron microscope [4,5] and more indubitable information about the local structure is expected. Such high resolution electron microscopy was applied to the investigation of the epitaxial crystallization of n-tetracontane crystals having such long spacing.

The other aim of this paper is to report a method to prepare well ordered

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n-tetracontane crystals, in which individual crystallite grows with the same orientation in a domain. This domain morophology is very suitable for the investigation of growth mechanism by high resolution electron microscopy, and especially for the investigation of coalescence, because the crystallites are expected to coalesce each other with the same crystallographic orientation.

EXPERIMENTAL

Thin crystalline film of n-tetracontane (n-$C_{40}H_{82}$) was obtained as an epitaxial film on freshly cleaved (001) of alkali halides, NaCl, KCl and KBr, by vacuum deposition at the base vacuum of 10^{-5} Pa. The n-tetracontane was supplied by Nakarai Chemical Co, Ltd. and its purity is about 99%. The substrate temperature of the alkali halides was kept at room temperature during the deposition after a preheat treatment at 400°C for 1 hour. The perheat treatment is considered to be effective for cleaning the substrate surface. The deposition rate of n-tetracontane was kept constant to be about 0.3 nm/sec. The grown thin n-tetracontane film was reinforced with thin carbon layer and was fixed on a Cu grid for electron microscopy after dissolving the substrate on water. High resolution imaging of lattice fringes and observation of morphology and diffaraction patterns were carried out with JEOL-2000FXII equipped with a minimum dose system[6] operated at 200 kV.

In order to examine the structural correlation between the epitaxial orientation of the deposited paraffin crystallites and the surface structure of the substrate, the substrate surface was decorated in advance with small gold particles by vacuum deposition and then the n-tetracontane was subsequently deposited on the decorated surface. The small gold particles with some nm in diameter were known to be preferentially crystallized on the surface steps of the substrate, which is known as the surface decoration.

RESULTS AND DISCUSSION

Epitaxial crystallization of paraffins on cleaved alkali halide surfaces by vacuum deposition has been studied by many researchers.[7] From these studies, it has been found that the close packed {110} of the paraffins lies parallel to the (001) surface of alkali halides and the chain molecules are mainly aligned along the lines of ions having the same charge in the substrate ⟨110⟩ directions.

In our case, n-tetracontane grew most regularly on KCl (001) surface. One example of high resolution electron diffraction pattern is shown in Fig. 1, which was obtained from a relatively wide area of the specimen grown on KCl. Diffraction spots of the long spacing along the c_s-axis of n-tetracontane are aligned along the [110] of KCl corresponding well to the result by Ueda et al.[8] One basic diffraction pattern of such orientation is indexed by the subcell Miller indices, h_s,k_s and l_s, as shown schematically in Fig. 2-a, and another companion diffraction pattern is overlapped orthogonally in Fig. 1. In addition to this epitaxial growth mode, a small part of the crystals was grown making its c_s-axis perpendicular to the substrate surface. The [110] of n-tetracontane

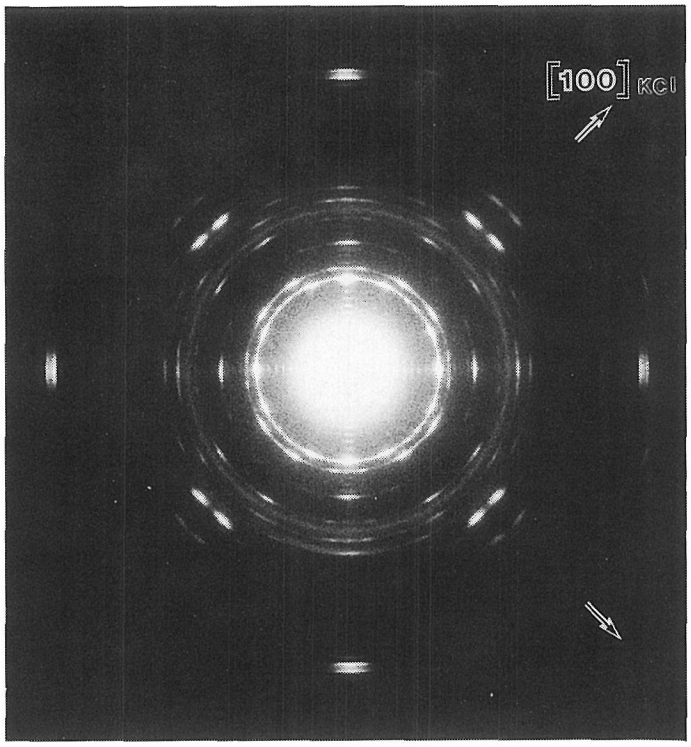

Fig. 1 High resolution electron diffraction pattern from the epitaxially grown n-tetracontane. Two kinds of epitaxy mode are observed: One is the major orientation mode where the chains align parallel to the substrate surface (see Fig.2-a) and the other is the minor one where the chains are perpendicular to the substrate surface (see Fig. 2-b).

orients along the [110] of the KCl substrate as shown in Fig. 2-b.

All reflections can be indexed by the orthogonal unit cell or subcell dimensions of $a=a_s=0.73$, $b=b_s=0.50$, $c=10.6$ and $c_s=0.25$nm.[9] This paper describes only about the former epitaxial mode where the chain axis orients parallel to the substrate surface. On NaCl and KBr, n-tetracontane was crystallized in a similar manner with the case on KCl, but the orientation relation with the substrate became worse and additional orientations appeared sometimes: for example, the chain aligns along the [100] of the substrate.

Typical morphology of the paraffin crystals grown epitaxially on the KCl surface is shown in Fig. 3, where small lath-shape crystallites are grown on the substrate surface and the shorter axis corresponds to the chain direction of n-tetracontane as shown later. A noteworthy point of the morphology is that the orientation of the crystallites is the same in a large domain, whose boundaries are indicated by the brocken lines in the figure. Such morphology is suitable for our present investigation, because we intended to investigate the epitaxial crystallization of paraffin on the substrate placing emphasis on the coalescence between crystallites during the crystal growth. The domain morphology shown in Fig. 3 enables us to investigate the coales-

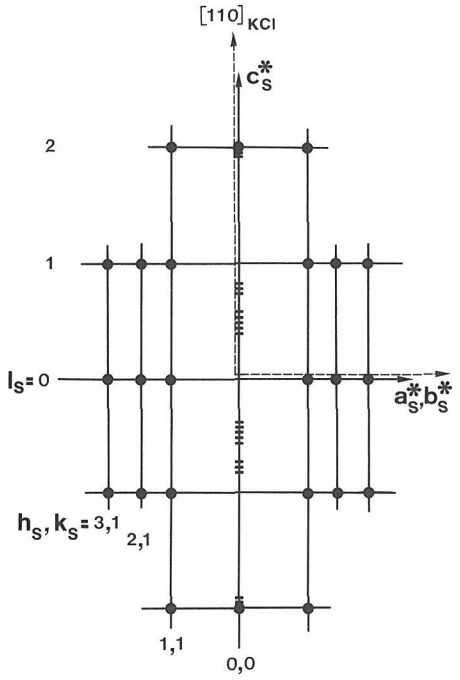

Fig. 2-a Schematic drawing of diffraction spots for the main epitaxy mode.

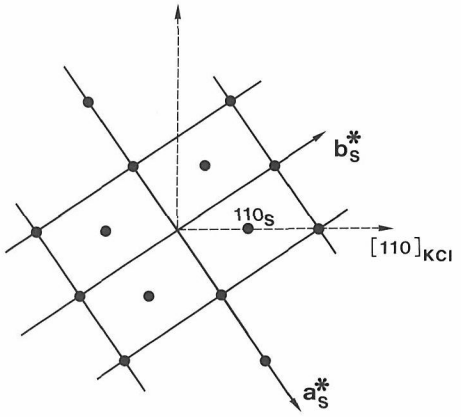

Fig. 2-b Schematic drawing of diffraction spots for the minor expitaxy mode

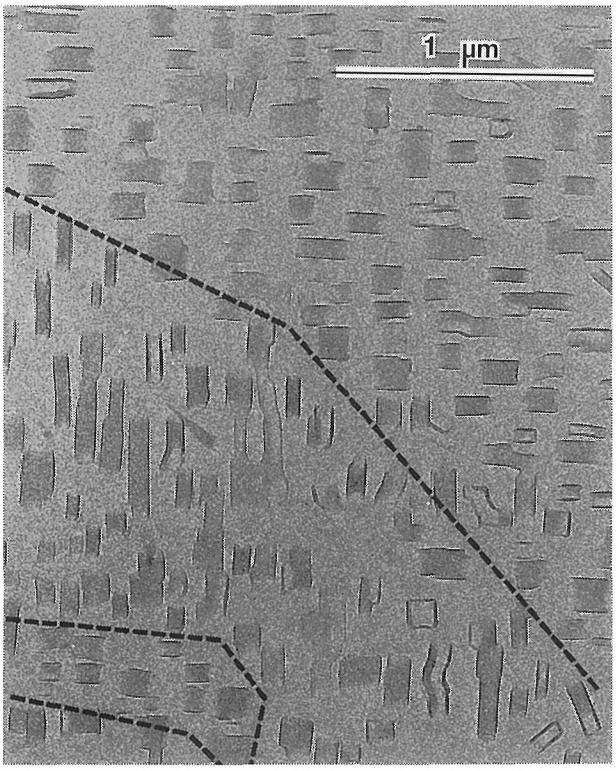

Fig. 3
Small lath-shape n-tetracontane crystallites grown on the (001) of KCl. The shorter axis corresponds to the chain direction. The orientation of the crystllites is found to be the same in one damain, whose boundary is shown by the brocken lines. Such domain morphology is characteristic on KCl.

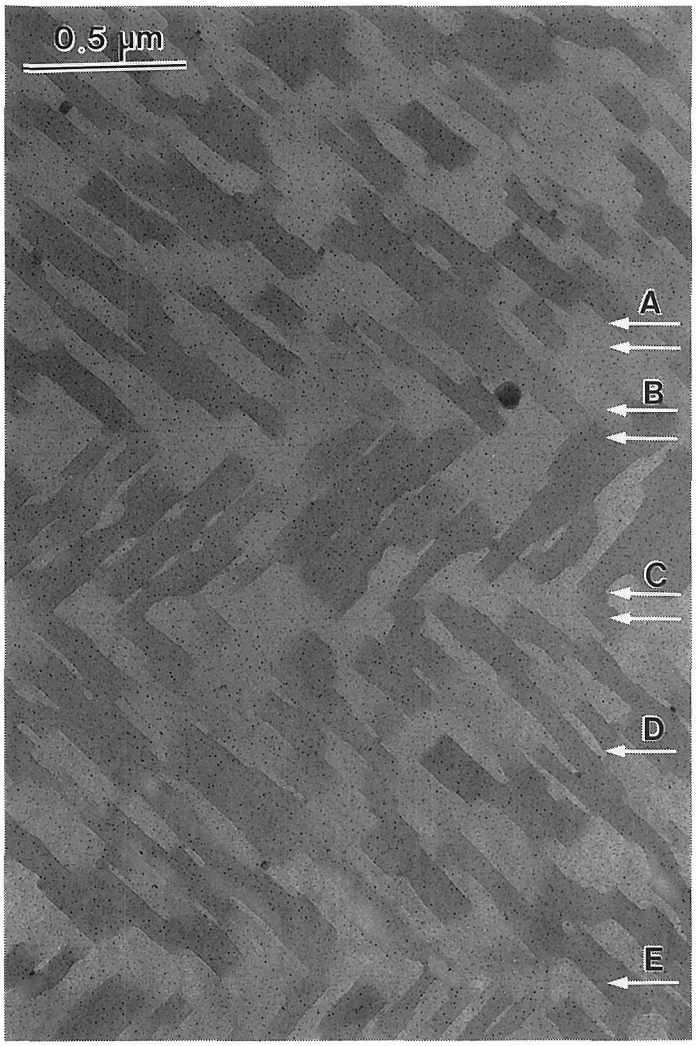

Fig. 4 The paraffin crystallites exhibiting the domain morphology on the KCl surface decorated with gold particles. The crystallites have only one orientation in one terrace bordered by gold decoration. Surprisingly the nucleation seems to occur on the terrace, but not at the step.

cence process of small crystallites growing with the same crystallographic orientation. On the contrary, such domain morphology was not observed on NaCl and KBr where each crystallite still grew epitaxially.

The origin of the domain morphology is not clear yet. However, one important point might be suggested by the following experiment. Before deposition of the paraffin, the substrate surface was decorated with small gold particles so as to relieve the surface steps of KCl. Even on such surface, the deposited paraffin grows epitaxially and exhibits the domain morphology as shown in Fig. 4. The figure shows a region of many [100] steps densely aligned on KCl substrates (shown by the white arrows). From Fig. 4, the paraffin crystallites change their orientation at the steps (in this figur, the

steps B, C and E). It is necessary to stress that the orientation of the crystallites does not always change at the steps, but the step exists where the orientation changes. That is, the crystallites have the same orientation on a terrace surrounded by steps.

From this fact, two mechanisms could be proposed for the formation of the domain morphology. The first is that the surface structure of the KCl substrate itself is altered from terrace to terrace: that is, a kind of surface reconstruction is different for each terrace after the present substrate treatment. Then the domain morphology might correspond to the decoration of surfaces with the organic molecules as proposed by Wittmann and Lotz[10] to specify a surface structure of talc. The second is that a very thin paraffin layer is quickly formed with one orientation on a terrace at the very early stage of the deposition and the many secondary nucleations occur sporadically in accordance with the orientation of the first layer, followed by the formation of the

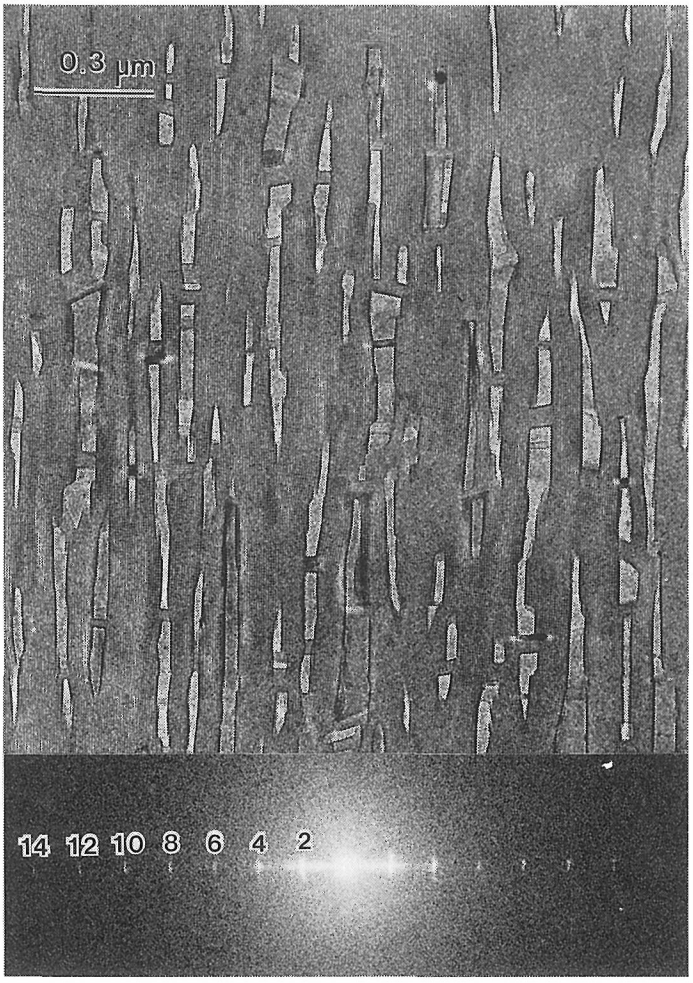

Fig. 5 A high resolution lattice image of well developed paraffin crystals, in which the 002-lattice fringes (spacing of 5.3 nm) are observed. Below, the corresponding optical diffractogram shows the diffraction spots up to the 14-th reflection.

domain morphology as shown in Figs. 3 and 4.

Some preliminary experiments showed that the nucleation might not start at the steps, but on terraces, and the domain morphology was not observed by the deposition at the vacuum worse than 10^{-1} Pa. These facts suggest that the epitaxial growth may be progressed on unusual surface structure of KCl. The further experiments will be needed to clarify the origin of the domain morphology.

High resolution observation was performed for these n-tetracontane crystals showing the domain mophology. An example of high resolution images is shown in Fig. 5, where paraffin crystals were well developed and already coalesced into longer crystals. This shows the image in one domain where the long crystals are running along a [110] of KCl substrate and interconnected inbetween with smaller crystallites. In the long crystals, 002-lattice fringes (spacing of 5.3 nm, which corresponds to the chain length) can be observed along the long direction of the crystals. The lower figure in Fig. 5 shows an optical diffractogram corresponding to the upper image. Diffraction spots up to 0 0 14 (0.76 nm in spacing) are clearly detectable. From the image it can be verified that the shorter axis of the lath-shape crystals corresponds to the c-axis as mentioned before.

Figure 6 shows an image of single-layer of the paraffin at edges of the paraffin crystals (indicated by the arrows) observed frequently in high resolution images. Such images of the single-layers were observed also in the case of cadmium arachidate thin

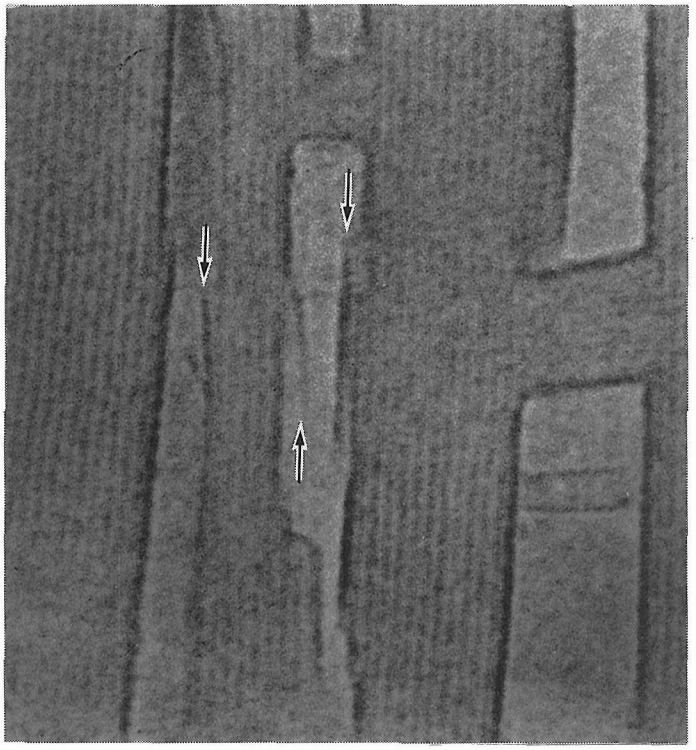

Fig. 6 Single-layer of molecules at edges of paraffin crystals indicated by the arrows.

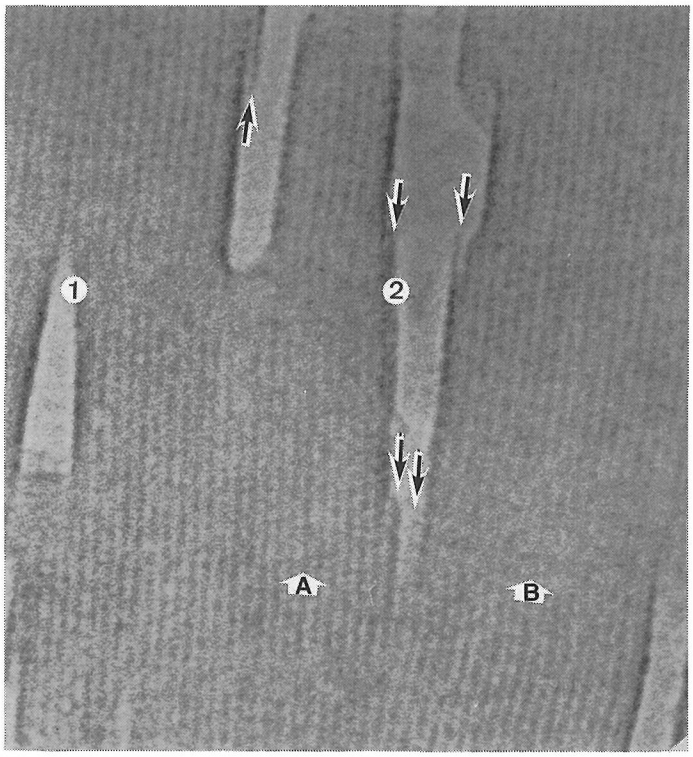

Fig. 7 Single-molecular steps at edges of paraffin as indicated by the arrows. Between the points 1 and 2, crystals of paraffin coalesce and the lattice planes are deformed, so that the lattice fringes are disappeared at the boundary.

film grown epitaxially.[11] They might be active growing sites in the crystallization. In some cases, such images of one molecular layer were observed apart from the mother paraffin crystal. Fig. 7 shows another example of such single-layer of molecules (indicated by the arrows in the figure). These figures support the step-by-step growth mechanism of the paraffin, which leads to the crystallite formation of the lath-shape as shown in Fig. 3.

Antoher noticeable point of Fig. 7 is the disappearance of the lattice fringes between the points 1 and 2, where two crystals coalesce from the opposite directions and the lattice planes are deformed on this line in order to adjust the two growing crystalline lattices in energetically favorite manner. Fig. 8 shows another image of coalescence, where A-crystal was growing upward and B- and C-crystals growing downward in the figure. On a line between the points 1 and 2, the lattice fringes are smeared and seem to be connected together so as to adjust two lattice planes smoothly. Before such coalescence, the lattice fringes in isolated crystals are observed always straight without any distortions. In Fig. 9, crystals are jointed each other on the lines connecting the points 1, 2, 3 and 4. Here again crystals seem to endeavor to joint each other smoothly to minimize the coalescence interfacial energy. Such coalescence mode is different from that of simple metals in which independently growing small crystals

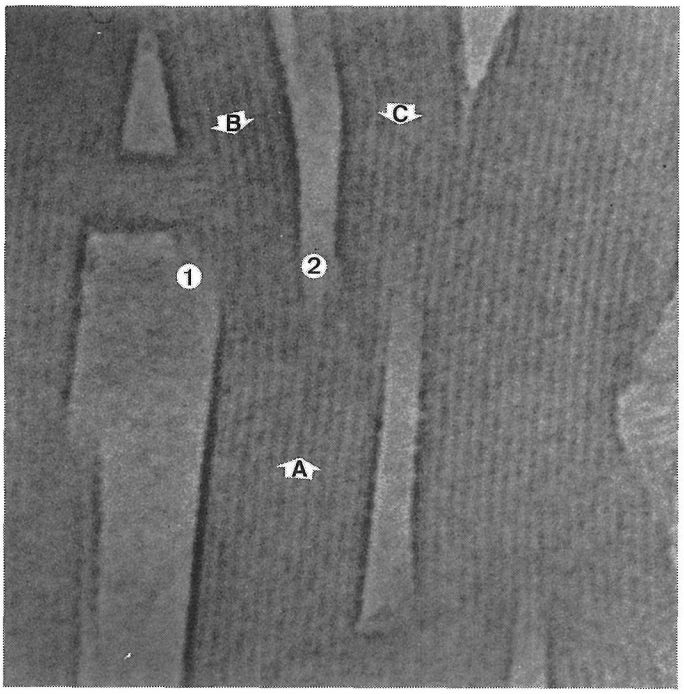

Fig. 8
The A- and B-crystals coalesce between the points 1 and 2, where the lattice fringes are smeared, but seem to adjust the lattice planes of two crystals smoothly.

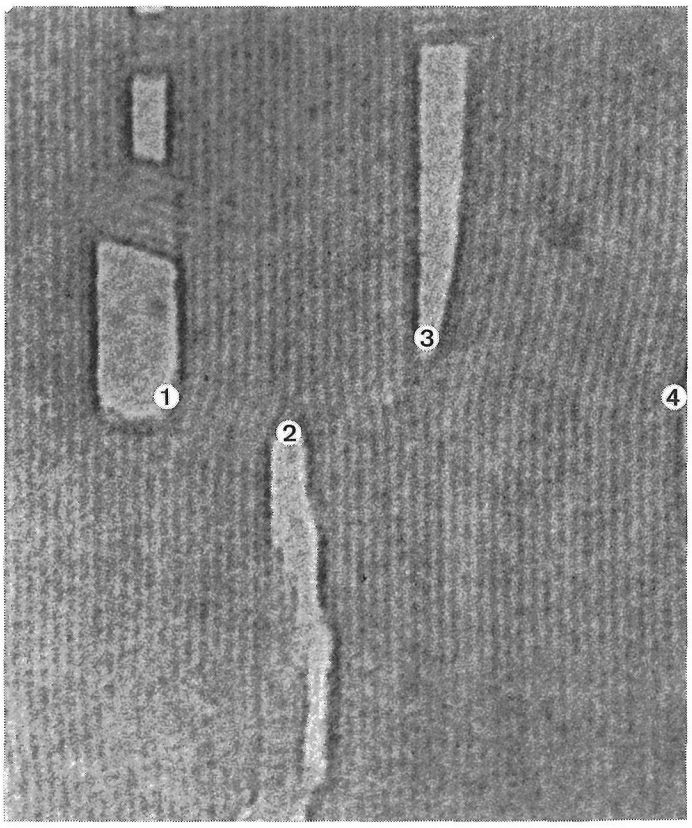

Fig. 9
Crystals coalesce each other on the lines connecting the points 1, 2, 3 and 4, where the crystals seem to endeavor to joint each other so as to minimize the coalescence interfacial energy.

are known to merge often into a large single crystal by rotational and/or translational rearrangements of every atoms on coalescence. On the contrary to this, the crystals of the paraffin do not change totally their orientations after coalescence, but only deform the lattice at the boundary to connect smoothly each other. This might come from the fact that it needs much energy to change their whole orientations for coalescing crystallites in the long chain compounds.

It has been reported that many stacking faults were frequently observed at coalescence boundaries, for example, in the cases of epitaxial growth of gold on MoS_2[12] and of phthalocyanines on alkali halides.[13] In the case of the paraffin, however, the coalescence boundary is not so sharp as the formation of stacking faults and the crystal lattices are moderately deformed in relatively wide region of the boundary. It may come from the fact that the paraffin is a more flexible crystal than metals or other rigid organic molecular crystals.

CONCLUDING REMARKS

Strange domain morphology of paraffin was obtained through epitaxial vapor deposition on KCl (001) and the formation of the domains is anticipated to be originated from the terrace structure surrounded by steps on the substrate.

In the crystallization of paraffin, the single-layer of the molecules was frequently observed and this supports the secondary nucleation on the surface of paraffin and the step-by-step growth mechanism. On the coalescence, two crystals seem not to collide or overlapped simply, but joint coherently without changing wholly their crystalline orientation. As a result, the crystal lattice is deformed at the interface so that the lattice fringes are smeared or disappeared at the interface.

More detailed studies are being carried out in order to clarify the mechanism of the domain morphology and to reveal the coalescence mechanism for various organic materials including the long chain compounds by high resolution electron microscopy.

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